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## ORGANIC DYE SENSITISERS FOR SOLAR CELLS AND SEMICONDUCTOR PHOTOCATALYSTS – A METHOD FOR SUITABILITY EVALUATION EXPLAINED

### ORGANICZNE BARWNIKI – SENSYBILIZATORY DO OGNIW SŁONECZNYCH I FOTOKATALIZATORÓW PÓŁPRZEWODNIKOWYCH – METODA OCENY PRZYDATNOŚCI Z WYJAŚNIENIEM

#### Abstract

Six polymethine dyes potentially suitable to use for dye sensitised solar cells and photocatalysts were studied. Electrochemical and spectral data have shown that LUMO levels of the dyes will provide high driving forces for electron injection ranging from 0.55 to 1.0 eV and only three dyes could be used with triiodide/iodide redox system applied for oxidised dye regeneration. The calculation method was explained in detail.

*Keywords: dye-sensitised solar cells, photocatalysis, polymethine dyes*

#### Streszczenie

Zbadano sześć barwników polimetynowych potencjalnie nadających się do użycia do baterii słonecznych i fotokatalizatorów sensybilizowanych barwnikami. Dane elektrochemiczne i spektralne wykazały, że poziomy LUMO barwników zapewnią wysokie siły napędowe dla przeniesienia elektronu, ale tylko trzy barwniki można użyć z systemem tryjodek/jodek stosowanym do regeneracji barwnika. Metodę obliczeniową szczegółowo objaśniono.

*Słowa kluczowe: ogniwa słoneczne sensybilizowane barwnikami, fotokatalizatory, barwniki polimetynowe*

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## 1. Introduction

Rapidly growing energy consumption raises concerns over ability to meet the future demands. It is expected that by 2050 the energy rate demand would double the today's figure of 15 terawatts ( $1.5 \times 10^{13}$  W). If we only had the technology, there would be no problem. The sun itself delivers on average 120 petawatts ( $1.20 \times 10^{17}$  W) of usable energy. New solar cells break records of energy conversion efficiency with 42.3% achieved by a triple junction cell of Spire semiconductor last year [1]. It uses InGaAs-GaAs-InGaP crystals. On the other hand, solar energy can be used not only to produce electric energy, but applied directly to drive chemical reactions. The idea is straightforward. Upon absorption of a photon the electron jumps from the valence band to the conduction band leaving a hole in the valence band. The excited electron is highly reactive and may form radicals that initiate further reactions. In the case of titanium dioxide, hydroxyl radicals are formed from a water molecule or hydroxide anion, or dioxygen is reduced to superoxide anion initiating reactions that lead to total oxidation of various organic substrates. The photon, however, must have the energy equal at least to the bandgap of the semiconductor. Catalytically active in this reaction may theoretically be mainly metal oxides, and as can be seen from Fig. 1 showing levels of bandgaps, all of them require for excitation the energy of 3.2 eV at least, which corresponds to the energy of UV radiation (390 nm). Because of that most of the solar energy would not be used. A solution to this problem is to use a sensitizer, a dye that would absorb light in the middle of the solar spectrum and have the energy of LUMO, into which the excited electron goes, above the level of the conduction band energy [2]. The idea is better explained in the diagram in Fig. 2.

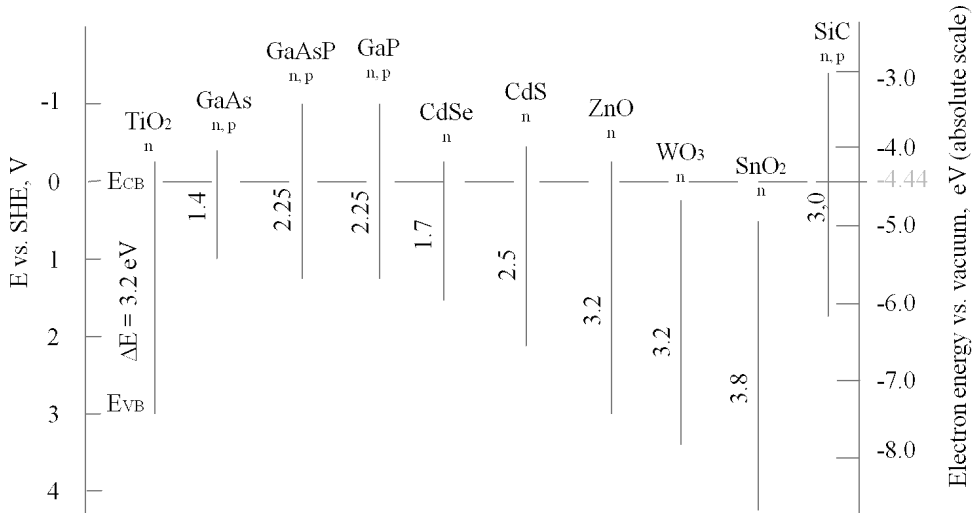


Fig. 1. Bandgaps and energies of valence and conduction bands of selected semiconductors [3]

Rys. 1. Szerokości przerwy wzbronionej i energie pasm walencyjnego i przewodnictwa wybranych półprzewodników

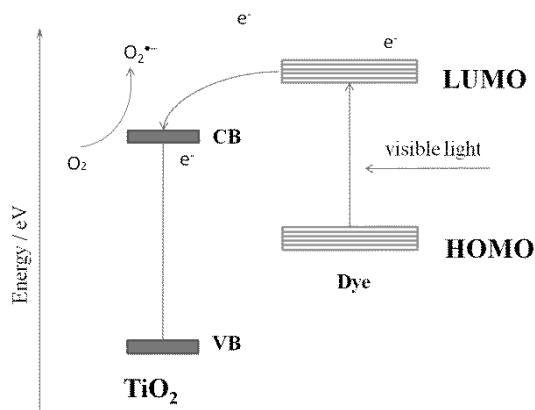


Fig. 2. The principle of dye-sensitised photocatalysis. Upon absorption of a photon, an electron is transferred from HOMO to LUMO of the dye. If the energy of LUMO is greater than the energy of the conduction band (CB) of the semiconductor, the electron may be injected into it. The energy of it is sufficient to produce active intermediates, like superoxide anion from dioxygen, as shown

Rys. 2. Zasada działania fotokatalizy z udziałem barwników-sensybilizatorów. W wyniku pochłonięcia fotonu elektron przechodzi z HOMO do LUMO barwnika. Jeśli energia LUMO jest większa od energii pasma przewodnictwa (CB) półprzewodnika, to elektron może tam wskoczyć. Energia jego wystarcza do wytworzenia aktywnych związków przejściowych, takich jak anion ponadtlenkowy z ditlenu, jak pokazano

Dye-sensitised solar cells are based on a similar principle. Suitable dyes must have LUMO energy level higher than the conduction band level of the semiconductor. Photoexcited electron is transferred to the conduction band then and from there it goes to the current collecting electrode. The semiconductor with the dye on its surface is immersed in a solution containing sort of a redox shuttle, a species with a redox potential slightly lower than the oxidation potential of the dye. This species reduced at the counter electrode travels to the oxidised dye to reduce it back to its original state, i.e. to regenerate it to enter again the cycle of converting light energy into electric energy. The principle of dye-sensitised solar cell operation is shown in Fig. 3.

The problem lies also in the conversion of energy levels. The energy levels of valence and conduction levels of semiconductors are usually given as the energy relative to vacuum (absolute scale) or sometimes as potential relative to a reference electrode used in electrochemical measurements depending on the method used for its determination. An electrode potential can be measured electrochemically versus a reference electrode, but the determination of the absolute value of an electrochemical electrode half-cell is experimentally unfeasible. However, its approximate value can be obtained from thermodynamic calculations, as recommended by IUPAC [4]. The calculations yield the value of  $4.44 (\pm 0.02)$  V as the absolute potential for the standard hydrogen electrode (SHE) at 298.15 K.

$$E^0(\text{H}^+/\text{H}_2)_{\text{H}_2\text{O}}(\text{abs}) = (4.44 \pm 0.02) \text{ V}$$

and consequently

$$E(\text{abs}) = E(\text{vs. SHE}) + 4.44 (\pm 0.02) \text{ V}$$

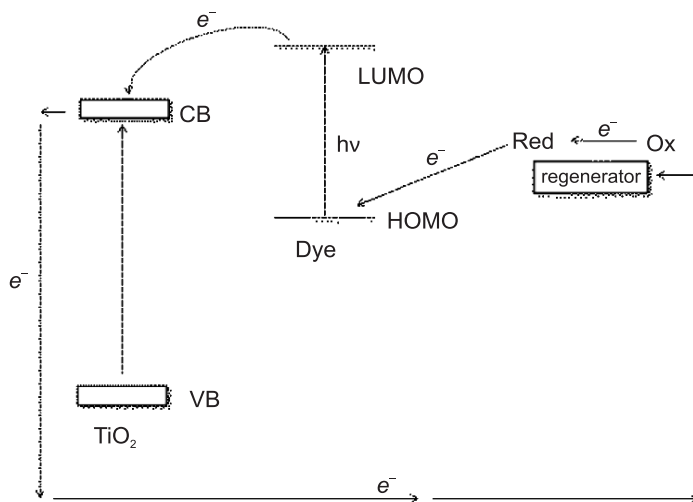


Fig. 3. Schematic diagram of a dye-sensitised solar cell

Rys. 3. Schemat ogniwa słonecznego z barwnikami sensybilizatorami

This equation cannot be directly used to measurements done in non-aqueous solvents. In such cases, particularly if an aqueous reference system was used, the measured potential includes also the liquid junction potential at the phase boundary between the aqueous and non-aqueous phases. Theoretically, it can be measured, sometimes even calculated yet inconvenient to do. IUPAC recommended to use ferrocenium<sup>+</sup>/ferrocene (Fc<sup>+</sup>/Fc) quasi-reference electrode in non-aqueous systems [5]. It is usually used as an internal standard. Potentials measured against this electrode can be converted to potentials vs. SHE by adding 0.400 V [6], the determined value of the standard potential for Fc<sup>+</sup>/Fc in water. It should be remembered though that this is only approximation as the real potential depends on the medium, though insignificantly.

$$E(\text{vs. SHE}) = E(\text{vs. Fc}^+/\text{Fc}) + 0.400 \text{ V}$$

It is generally assumed that an electron goes to LUMO upon electroreduction, and is removed from HOMO upon oxidation [7–9]. The values of HOMO and LUMO obtained from electrochemical measurements usually differ by about 0.1 to 0.6 V from those obtained in experiments *in vacuo* (e.g., ionisation potential), which is mainly due to solvation energy of ions. Moreover, the difference of LUMO-HOMO calculated from spectroscopic data is not exactly equal to the value obtained from electrochemical data, which is again chiefly caused by the fact that the molecule is not ionised upon photoexcitation and hence solvation energies may differ. Another plausible reason is that the electron may be transferred not to LUMO but to a higher orbital or to a combined orbital, or as indicated by Franck-Condon principle it goes to a higher vibrational energy level. Better fits may be obtained from fluorescence spectra.

$$E_{\text{HOMO}} = e \cdot E_{\text{ox}} - \Delta E_{\text{sol}} + \text{constant}$$

and

$$E_{\text{LUMO}} = e \cdot E_{\text{red}} - \Delta E_{\text{sol}} + \text{constant}$$

$E_{\text{ox}}$  and  $E_{\text{red}}$  denote oxidation and reduction potentials converted to the value in vacuum (absolute scale) as explained above (unless this conversion is hidden in the constant),  $e$  denotes the electron charge. Please note that it is negative and changes the sign of the energy. Most convenient is to use just  $-1$  as a the unit of charge and to express the potentials in volts. Then the result is in electron-volts (eV).

Usually even the calculation of solvation energy is omitted and  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$  are calculated by direct multiplying the  $E_{\text{ox}}$  and  $E_{\text{red}}$  converted to the absolute values (in vacuum) as above by  $-1$  (effectively changing the sign) and obtaining HOMO and LUMO expressed in electron-volts.

An n-type semiconductor, like  $\text{TiO}_2$ , needs a dye that might be capable of transferring an electron to its conduction band upon photoexcitation, which means, from the dye's LUMO. The usual practice in this case, however, is to calculate the energy level of LUMO from the energy level of HOMO and adding to it the energy of the absorbed light calculated from the UV-Vis spectrum of the dye. This method should give more reliable results. Thus,

$$E_{\text{LUMO}} = e \cdot E_{\text{ox}} + h\nu = e \cdot E_{\text{ox}} + c/\lambda$$

where  $c$  is the speed of light and  $\lambda$  is the wavelength of the absorbed light.

Then it is enough to check whether the calculated value of  $E_{\text{LUMO}}$  is higher than the  $\text{TiO}_2$  conduction band level. If so, then it is thermodynamically possible for an electron from the photoexcited dye to go to the conduction band of the semiconductor, i.e., to act as a sensitizer. The dye should advantageously absorb light somewhere in the middle of the sun radiation spectrum reaching the earth's surface, between 500 and 750 nm, where  $\text{TiO}_2$  does not absorb.

There are other problems concerning the details of calculations. The energy levels are usually energy bands, light is absorbed not only at the band peak wavelength but all over the band with a characteristic Gaussian bell shape. The same concerns electrode reactions that occur not only at (or beyond) their peak or  $E_{1/2}$  (or standard potential) values but over all the voltammetric curve. Instead of peak or standard values, the values of the onset potential or of the optical band onset at the side of lower energies – higher wavelengths, where formally the process begins, may be used.

The energy gap in amorphous semiconductors is usually determined from optical absorption spectra using a Tauc plot [10], square root of the absorption coefficient multiplied by photon energy  $(\alpha h\nu)^{1/2}$  as a function of photon energy  $h\nu$ . The plot is usually linear and extrapolating it to the baseline yields the onset of absorption. This should be equivalent to the distance between the band edges.

It is thus natural to use consequently such an approach in the calculations of the dye parameters, which means that the onset potential of the first oxidation process should be used as  $E_{\text{ox}}$  and the optical band onset at the side of higher wavelengths should be used for  $h\nu$  (LUMO-HOMO gap) calculations.

An analogous problem occurs in the case of polymer light emitting diodes, where it is important to match cathode work function to the  $\pi^*$  – band energy and the anode work function to the  $\pi$ -band energy level. Some authors simply did not pay attention to the origin of their data and mixed figures derived from spectral peak energies or  $E_{1/2}$  electrochemical

potentials (corresponding to standard potentials) with those derived from the optical band onsets or onset potentials. To put some order to this, energy gaps for polymers used calculated from electrochemical data using either  $E_{1/2}$  or onset potentials were compared with those calculated from spectroscopic data with peak or band onset wavelengths. It was clearly demonstrated that they could be matched pairwise, optical energy gaps derived from band onset wavelengths were practically equal to electrochemical energy gaps derived from onset potentials and those based on peak energies equal to those calculated from  $E_{1/2}$  values [11].

A very similar situation exists in dye-sensitised solar cell area. Authors use values based on peak energies mixed with those derived from onset potentials in their calculations. Sometimes realising that onset values are needed they call data based on peak values, which can clearly be seen from comparison of the data in the text and those seen in figures. That is why there is a need to explain the basis of the calculations used for the evaluation of the dyes.

Here we present electrochemical and spectroscopic data for examples of cationic polymethine dyes with indoline end groups and anionic polymethine dyes with trioxo- or dioxothio-hexahydropyrimidinylidene end groups and their HOMO and LUMO energies calculated from both the peak and onset values.

## 2. Experimental

Dye samples were generously donated by Prof. A.A. Ishchenko from the Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Kyiv [12].

Cyclic voltammetry measurements were done using a BAS 100B/W Electrochemical Workstation with a C3 Cell Stand (Bioanalytical Systems) with a standard three-electrode cell. The working electrode was a 1.6 mm diameter glassy carbon electrode (Mineral) and platinum wire was the auxiliary electrode. All potential were measured and quoted against an Ag/AgCl (3 M NaCl) electrode that was put into a double bridge filled in the upper part with 3 M NaCl solution and in the lower part with supporting electrolyte solution, both solutions being separated by a cotton wool plug, and parted from the test solution by a dense ceramic frit. 0.1 M tetra-n-butylammonium tetrafluoroborate solution in methanol (Chempur) was employed as the supporting electrolyte solution. It was additionally dried with 4A molecular sieves. All measurements were done under dry argon atmosphere. Voltammograms were registered at 100 mV s<sup>-1</sup> scan rate unless otherwise noted.

Onset potentials were calculated from the point of intersection of the tangent to the voltammetric wave at its inflection point with the baseline. The position of the inflection point was taken from the maximum of the first derivative of voltammogram using the built-in function and the value of the first derivative was taken as the slope of the tangent at the inflection point.

Spectra were recorded with a fibre optics OceanOptics USB 2000-XR spectrometer.

### 3. Results

Three cationic polymethine dyes with indoline end groups (indoline carbocyanine dyes) with two to four methine groups were taken for the studies. Their structures and codes are shown below.

Cyclic voltammetry shows (Fig. 4) distinct oxidation and reduction processes for all the three dyes. The waves on the forward scans indicate that they are diffusion controlled, and hence the electrode process is rapid. Thus, despite the fact that the processes cannot be regarded reversible owing to the lack of the corresponding reverse process, the data from the forward process may be used for the calculation of thermodynamic parameters. This is confirmed by the deconvoluted voltammogram (Fig. 5), in which corresponding waves

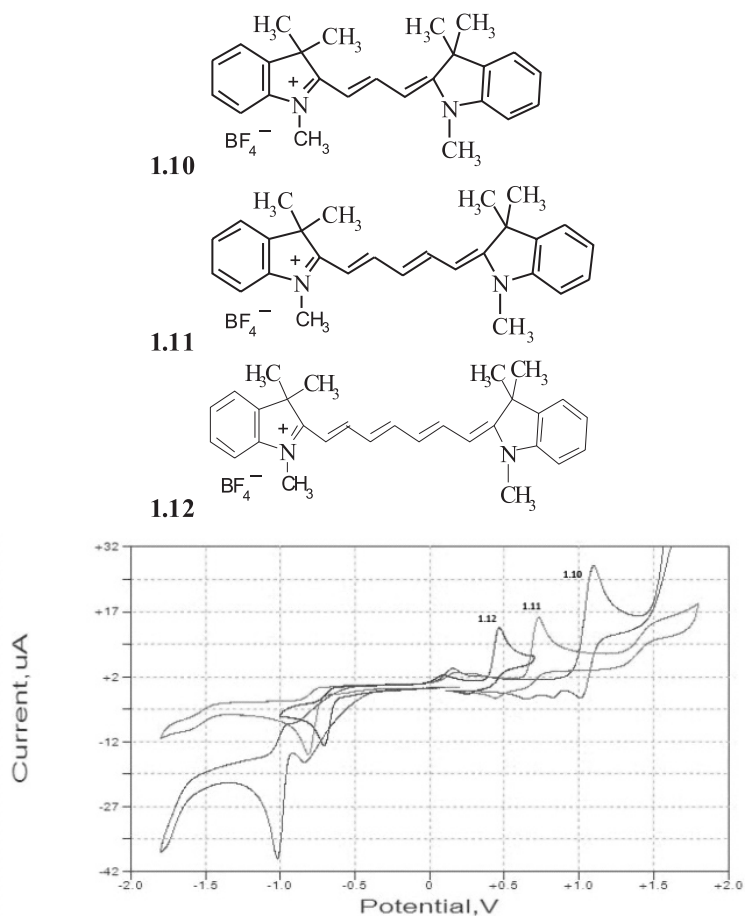


Fig. 4. Cyclic voltammetry of 1.10, 1.11 and 1.12 dyes

Rys. 4. Woltamperometria cykliczna barwników 1.10, 1.11 i 1.12

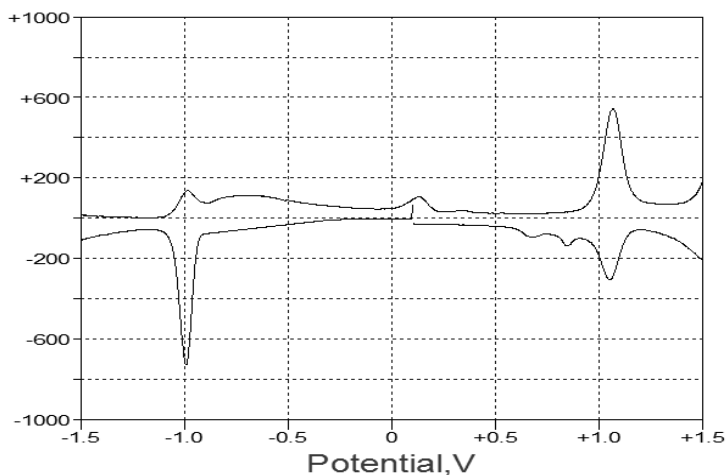


Fig. 5. Semi-derivative deconvolution of voltammogram of carbocyanine dye 1.10

Rys. 5. Woltamperogram barwnika karbocyjaninowego 1.10. po dekonwolucji semi-różniczkowej

appear on the reverse scan. Their intensity is obviously low, but the peaks on the forward and reverse scans are at the same potential.

The lack of the waves for the corresponding process and the presence of a couple of smaller cathodic waves instead indicate that the product of oxidation is unstable and decomposes into several products. A similar image can be seen for reduction, yet in this case only one smaller wave is observed. This does not mean that the dye cannot be used as a sensitizer, because in the working system the oxidation product may be reduced much faster than on the voltammetry time scale, and the decomposition products may also be redox active.

Spectra of the studied carbocyanine dyes (Fig. 6) exhibit one band with a shoulder in the visible region. The longer the bridge, the lower the energy of photons absorbed.

Comparison of the three dyes of the same structure but with a bridge with different number of  $-\text{CH}=\text{CH}-$  units indicates that the longer the bridge, the shorter differences between the first oxidation and reduction potential, which has been expected given that they are related to HOMO and LUMO energy levels and the same is observed in the spectra.

In an analogous manner were studied three further polymethine dyes, trioxo- and dioxothio-hexahydropyrimidinylidene derivatives, the structures and codes of which are presented below.

These three dyes can be characterised very similarly to the above discussed carbocyanine dyes. It is somewhat surprising that substitution of one oxygen atom for sulphur has practically no effect whatsoever on the spectra and redox potentials. Oxidation potentials are lower compared to the above discussed carbocyanine dyes. Certainly, the fact that carbocyanine dyes were in the cationic form contributed to that effect.

The data for the dyes investigated are summarised in Tables 1 and 2.



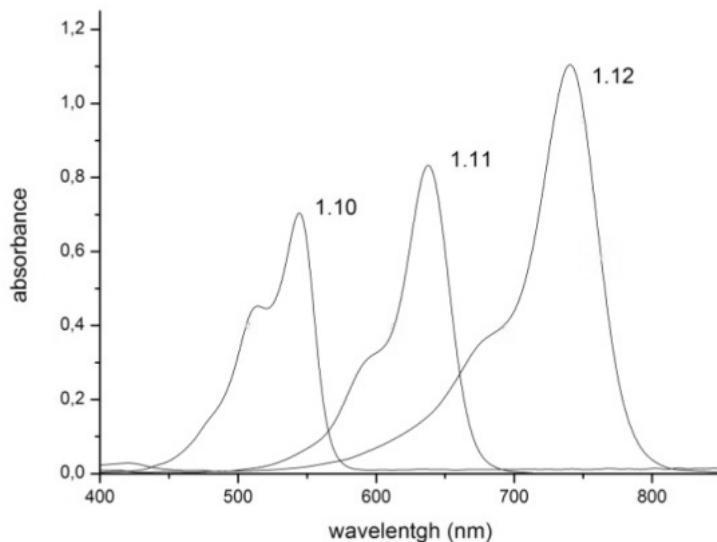


Fig. 6. UV-vis spectra of the studied carbocyanine dyes

Rys. 6. Widma UV-vis badanych barwników karbocyjaninowych

Table 1

**Summary of spectral and electrochemical data of the studied dyes based on peak and standard potential ( $E_{1/2}$ ) values.  $\Delta E$  is the difference between the energy of light absorbed and the reduction and oxidation potentials multiplied by the electron charge**

Dye	Spectral data		Electrochemical data (vs. SHE)			Difference $\Delta E$ , eV
	$\lambda_{\max}$ , nm	$h\nu$ , eV	$E_{1/2 \text{ ox}}$ , V	$E_{1/2 \text{ red}}$ , V	$e(E_{1/2 \text{ red}} - E_{1/2 \text{ ox}})$ , eV	
1.10	545	2.27	1.020	-1.035	2.11	0.16
1.11	637	1.95	0.653	-0.815	1.54	0.41
1.12	740	1.68	0.403	-0.710	1.17	0.51
bm3	536	2.31	0.366	-0.953	1.81	0.50
etb3	535	2.32	0.718	-1.025	1.80	0.52
bm5	586	2.12	0.729	-1.020	1.37	0.75

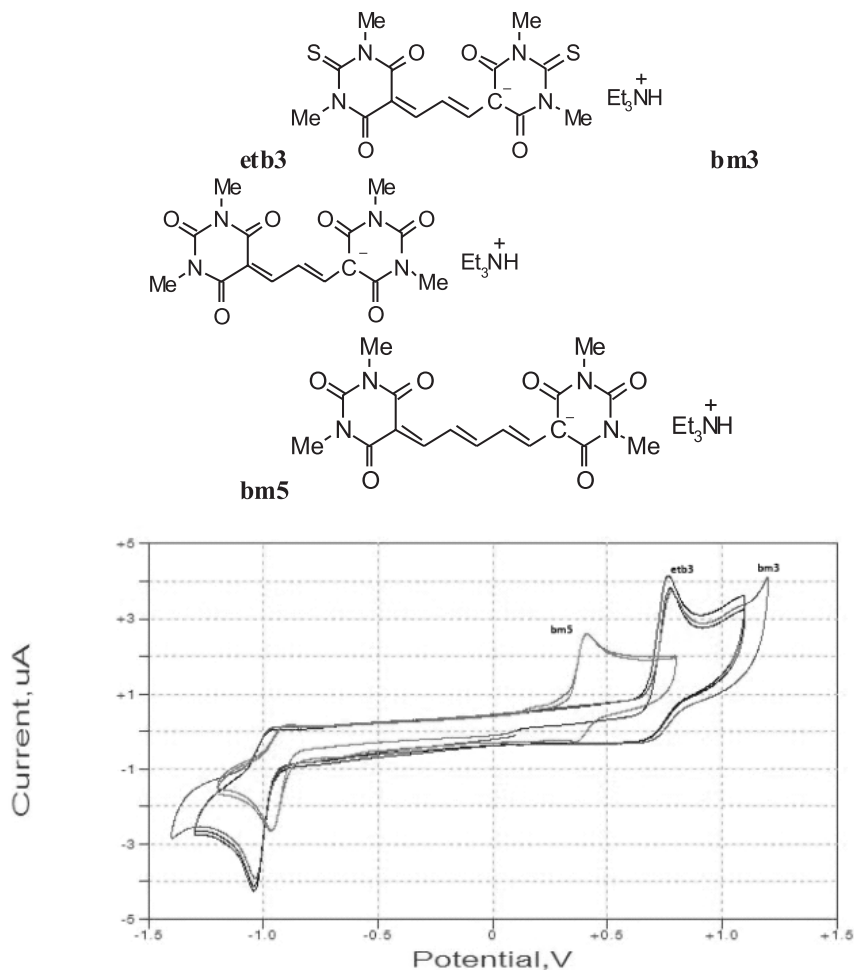


Fig. 7. Cyclic voltammograms of etb3, bm3 and bm5 dyes

Rys. 7. Woltamperogramy barwników etb3, bm3 i bm5 dyes

As discussed in Introduction, owing to the fact that bandgap energy values were obtained from band onset data, it would be more appropriate to use similar data for the dyes for the calculation of their HOMO and LUMO levels. Upon absorption of a photon by the dye molecule, an electron is transferred from HOMO to LUMO. Following this path, the LUMO was calculated by adding the  $h\nu$  energy of the photon at the band onset to the HOMO energy level that was calculated in turn from the onset potential of oxidation.

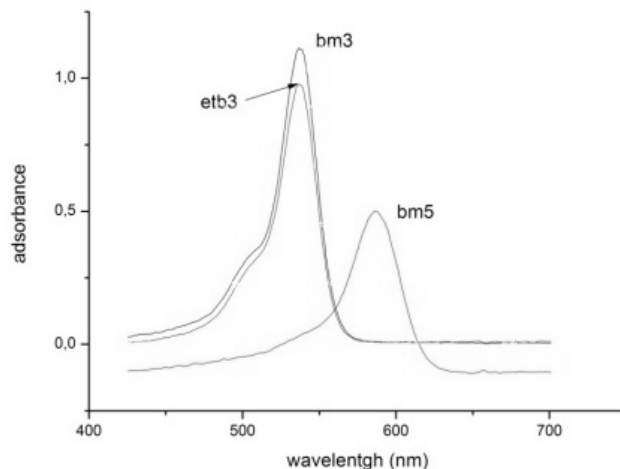


Fig. 8. Spectra of etb3, bm3 and bm5 dyes

Rys. 8. Widma barwników etb3, bm3 and bm5 dyes

Table 2

**Summary of spectral and electrochemical data based on onset potentials and band onsets at the side of higher wavelengths (lower energy).  $\Delta E$  is the difference between the energy of light absorbed and the reduction and oxidation potentials multiplied by the electron charge**

Dye	Spectral data		Electrochemical data (vs. SHE)			Difference $\Delta E$ , eV
	$\lambda_{\text{onset}}$ , nm	$h\nu$ , eV	$E_{\text{onset ox}}$ , V	$E_{\text{onset red}}$ , V	$e(E_{\text{onset red}} - E_{\text{onset ox}})$ , eV	
1.10	565	2.19	0.990	-0.927	1.98	0.21
1.11	673	1.84	0.629	-0.699	1.41	0.43
1.12	785	1.58	0.369	-0.611	1.05	0.53
bm3	563	2.20	0.322	-0.876	1.65	0.55
etb3	567	2.19	0.689	-0.956	1.67	0.52
bm5	622	1.99	0.676	-0.952	1.22	0.77

Table 3 summarises HOMO and LUMO energies calculated from data of Table 2 as discussed above. It appears that all the calculated LUMO energies are higher than the conduction band energy of  $\text{TiO}_2$ . The highest difference is observed for bm5 dye. On the other hand such high values of the driving force are excessive and mean that a significant portion of solar energy will be lost. Best known sensitizers based on ruthenium complexes used in solar cells, like N719, N3 or N749, are probably more efficient with the driving force for electron injection of only ca. 0.15 eV, which was proven to be a sufficient value [2]. The studied dyes may, however, be applied in solar cells based on other semiconductors with much higher lying conduction bands (Fig. 1).

**HOMO and LUMO energy levels of the studied dyes and driving forces for electron injection from LUMO to TiO<sub>2</sub> conduction band, and for oxidised dye regeneration by I<sub>3</sub>/I<sup>-</sup> couple**

Dye	HOMO, eV	LUMO, eV	Driving force for electron injection from photoexcited dye to TiO <sub>2</sub> conduction band*, eV	Driving force for oxidised dye regeneration by I <sub>3</sub> /I <sup>-</sup> couple**, eV
1.10	-5.43	-3.24	0.54	0.484
1.11	-5.07	-3.23	0.55	0.117
1.12	-4.81	-3.23	0.55	-0.133
bm3	-5.12	-2.92	0.86	-0.170
etb3	-5.13	-2.94	0.84	0.182
bm5	-4.76	-2.77	1.01	0.193

\* Driving force for electron injection from photoexcited dye to TiO<sub>2</sub> conduction band was calculated as the difference of the conduction band energy of -3.78 eV minus the energy of LUMO.

\*\* Driving force for oxidised dye regeneration was calculated as the difference of standard redox potential of I<sub>3</sub>/I<sup>-</sup> couple of 0.536 V minus  $E_{1/2\text{ox}}$  from Table 1 multiplied by the electron charge.

Another parameter of interest in the case of solar cells is the possibility to regenerate the dye molecule after it had injected an electron to TiO<sub>2</sub>. The most popular system used for the regeneration is triiodide/iodide redox couple. For the iodide to reduce the oxidised dye, the redox potential of iodide must be lower than the oxidation potential of the dye, and because the iodide anion oxidation to triiodide requires two electrons, it is associated with a higher energy barrier and hence a minimum driving force of 0.2 to 0.3 eV is needed [2]. As the standard redox potential of I<sub>3</sub>/I<sup>-</sup> couple is available, to match it,  $E_{1/2\text{ox}}$  for the dye from Table 1 is used in calculations. The results gave two negative values, for 1.12 and bm3 dyes. These two dyes are therefore unsuitable for use in solar cells with triiodide/iodide redox couple used for regeneration. The driving force for 1.11, though positive, seems to be definitely too low.

Though intrinsically simple, the method of HOMO and LUMO calculation involves many steps and may seem obscure. That is why it will be explained in detail step by step.

Potentials in non-aqueous solutions are measured against aqueous reference electrodes. At the phase boundary, a potential difference will develop, due to different concentrations and different solvation energies in two different solvents. That means that the measured potential includes the liquid junction potential, the value of which is unknown. The best solution is to use a universal internal standard, like ferrocene (Fc), the oxidation potential of which is known to not be affected by the type of solvent [5]. Its redox potential vs. standard hydrogen electrode (SHE) in aqueous solutions is known and equal to 0.400 V. So first, the measured potential, in our case vs. Ag/AgCl electrode, should be converted to the potential vs. Fc<sup>+</sup>/Fc. All the values are expressed in volts.

$$E_{\text{ox}}(\text{vs. Fc}^+/\text{Fc}) = E_{\text{ox}}(\text{vs. Ag/AgCl}) - E_{1/2\text{ox}}(\text{ferrocene vs. Ag/AgCl})$$

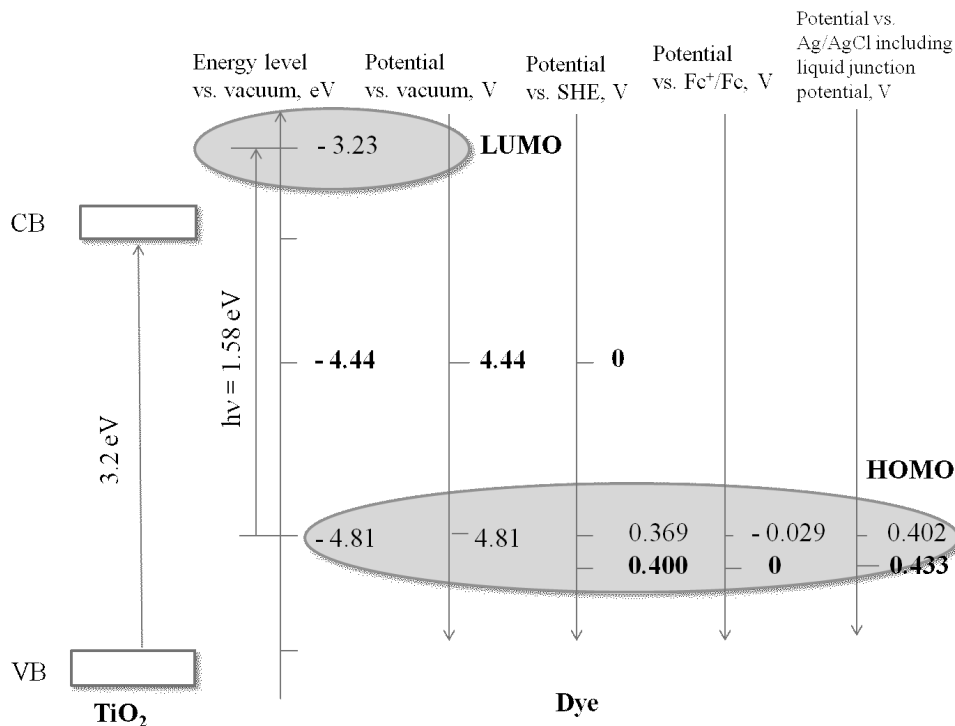


Fig. 9. Calculation of HOMO and LUMO energies for 1.10 dye step by step, explained in the text. Bold figures refer to reference potentials. Please note that arrows for potential scales point downwards as in this direction potential increases. The arrow for energy points upwards in the direction of rising values of energy

Rys. 9. Wylczenie energii HOMO i LUMO dla barwnika 1.10 krok po kroku z wyjaśnieniami w tekście. Liczby wytłuszczone odnoszą się do potencjałów odniesienia. Proszę zwrócić uwagę na to, że strzałki dla skal potencjałów są zwrócone w dół, ponieważ w tym kierunku potencjał wzrasta. Strzałka dla energii jest zwrócona w górę w kierunku wzrastających potencjałów

$E_{1/2, \text{ox}}$  for ferrocene oxidation measured under the same conditions, added as an internal standard, is used for the calculations. It is determined for each solution separately.  $E_{1/2, \text{ox}}$  is used in this case, as also the Fc<sup>+</sup>/Fc potential vs. SHE applied further on, is the standard potential for this reaction.

Then, the potential vs. Fc<sup>+</sup>/Fc is converted to the value versus standard hydrogen electrode.

$$E_{\text{ox}}(\text{vs. SHE}) = E_{\text{ox}}(\text{vs. Fc}^+/\text{Fc}) + 0.400$$

Although it is not possible to measure directly or even accurately calculate the potential of SHE in vacuum, or in other words, the absolute potential of it, its approximate value may be obtained from thermodynamic data, and it was accepted by IUPAC that the best approximation for this potential is 4.44 V [4]. Thus,

$$E_{\text{ox}}(\text{vs. vacuum}) = E_{\text{ox}}(\text{vs. SHE}) + 4.44$$

This is the value of the potential. The energy is equal to the product of the charge and the potential. We are discussing the energy of electrons and, consequently, the potential has to be multiplied by the electron charge. The simplest way is to use the atomic units and the electron charge is equal  $-1$ . The energy thus obtained is in electron volts, eV. The numerical result is the same figure but with the opposite charge.

$$E(\text{HOMO}) = e \cdot E_{\text{ox}}(\text{vs. vacuum})$$

Oxidation potentials against vacuum potential are generally positive and HOMO energies are generally negative. It is the result we expect as in molecules electrons are somewhere near the positively charged core or nucleus.

LUMO energy might be calculated by adding the energy of photon,  $h\nu$ , or  $h/\lambda$ .

$$E(\text{LUMO}) = E(\text{HOMO}) + h/\lambda.$$

The method is illustrated in Figure 9.

#### 4. Conclusions

All the studied polymethine dyes exhibited similar characters of cyclic voltammetry and spectra. They showed both cathodic and anodic waves, the distance between which depended on the length of the methine bridge. In the visible region they had one band with usually one shoulder. The energy of the band correlated with the length of the methine bridge.

It was shown that all the studied dyes have their LUMO levels at higher energies than the conduction band of  $\text{TiO}_2$  and thus may be used as sensitizers for  $\text{TiO}_2$ . However, the driving forces for electron injection from photoexcited dye are excessively high and may result in significant energy losses. Three of the studied dyes exhibit too low oxidation potentials to be regenerated after electron injection by triiodide/iodide redox couple and thus seem unsuitable for solar cells using this redox system.

Based on electrochemical redox potentials determined from cyclic voltammetry results it is possible to calculate HOMO and LUMO levels. The differences in the values thus obtained for the studied dyes agree only very roughly with the HOMO-LUMO differences obtained from spectral data. This results most probably from different environments used in these two techniques.

It is more natural to use data obtained in a similar manner for related calculations. As the bandgaps of semiconductors are generally obtained using Tauc type plots, which are based on band onsets, it is recommendable to use also onset potentials in such calculations.

HOMO level energies may be calculated from first oxidation potentials of dyes, and it is better to obtain LUMO levels by adding the photon energy to HOMO level.

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